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The Electron Affinity of Bromine and a Study of Its Decomposition on Hot Tungsten* **

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The electron affinity of bromine has been measured by determining the ratio of ions to electrons leaving a hot tungsten surface in contact with bromine gas at low pressure. The value obtained is 80.5±0.4 kcal./mole. The measurements, which extend over a range of 700° in temperature and 80-fold in pressure, show no trend in the electron affinity and demonstrate that the decomposition of bromine under these conditions is a first-order reaction. The assumption of unit accommodation coefficient is shown to be correct.

INTRODUCTION

THE electron affinity is defined as the energy change $(-\Delta E_0)$ accompanying the union of an electron and an atom at absolute zero. Thus the electron affinity corresponds precisely to the ionization potential of its univalent negative ion. In contrast to the complete tables of ionization potential (electron detachment) of atoms there exists only a small number of less accurately determined electron affinities (electron attachment). The small number of values reflects the small number of stable negative monoatomic ions, while the lack of accuracy indicates the absence of spectroscopic measurements. The general agreement that the capture of electrons by atoms with the simultaneous emission of radiation is an improbable event accounts for the failure of spectroscopists to measure directly electron affinities. Indirect spectroscopic measurements are uncertain.

This investigation is concerned with the direct measurement of the electron affinity of bromine by a refinement of the method of Sutton and Mayer,[1] which permits increased precision and an extension of the measurements to larger ranges of temperature and pressure.

PRINCIPLE OF THE METHOD

By a suitable experimental arrangement (see Apparatus) it is possible to measure the ratio of bromine ions to electrons leaving the surface of a hot tungsten wire surrounded by bromine at a constant pressure. This ratio, together with the pressure of bromine and the temperature of the wire, is sufficient to calculate the equilibrium constant and hence the energy change (the electron affinity) of the reaction

$$Br + e \rightarrow Br^- . \qquad (1)$$

The assumption must be made in such a calculation that all the bromine molecules which hit the hot filament come to thermal equilibrium with the filament and dissociate and ionize accordingly. Then it follows that the number of

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[1] P. P. Sutton and J. E. Mayer, J. Chem. Phys. **3**, 20 (1935).

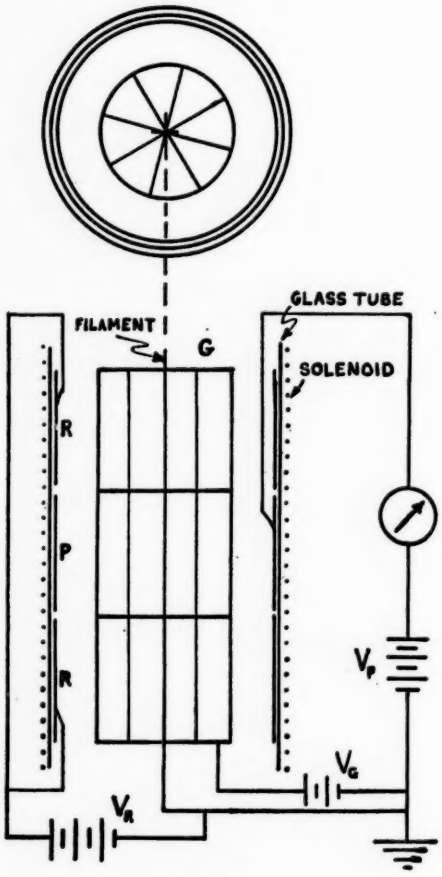

FIG. 1.

bromine atoms leaving the filament is related to the pressure P_{Br} of bromine atoms in a gas at the same temperature as, and in equilibrium with, the surface by

$$Z_{Br}=\frac{P_{Br}}{(2\pi m_{Br}kT_s)^{\frac{1}{2}}}, \tag{2}$$

where T_s is the temperature of the surface. If the temperature of this surface corresponds to virtually complete dissociation of bromine (greater than 1500°C) at existing pressures and if a negligible fraction of the atoms are converted into ions (which is true in this case), then one may equate the number of molecules hitting to half the number of atoms leaving the surface. This yields the expression

$$P_{Br}=P_{Br_2}(4m_{Br}T_s/m_{Br_2}T_r)^{\frac{1}{2}}=\sqrt{2}P_{Br_2}(T_s/T_r)^{\frac{1}{2}}, \tag{3}$$

where P_{Br_2} is the pressure of Br_2 surrounding the filament at temperature. The ion-electron ratio can be used as follows to obtain an expression for the pressure ratio

$$P_{Br^-}/P_e=(i_{Br^-}/i_e)(m_{Br}/m_e)^{\frac{1}{2}} \tag{4}$$

of ions and electrons in the hypothetical equilibrium gas.

Combining (3) and (4) the equilibrium constant and the standard free energy change of the reaction (1) may be written as

$$K=\exp(-\Delta F^0/RT_s)=P_{Br^-}/P_eP_{Br}$$
$$=(1/\sqrt{2})(i_{Br^-}/i_e)(1/P_{Br_2})(m_{Br_2}T_r/m_eT_s)^{\frac{1}{2}}. \tag{5}$$

The standard free energy change is related to the electron affinity ($-\Delta E_0$) by the equation

$$-\Delta E_0=-\Delta F^0(T)$$
$$+F^0_{Br^-}(T)-F^0_e(T)-F^0_{Br}(T). \tag{6}$$

Since the free energy of each of the species is given by

$$F^0(T)=RT\ln(h^2/2\pi mkT_s)^{\frac{1}{2}}(1/kT_sQ') \tag{7}$$

at unit pressure, Eq. (6) may be written as

$$-\Delta E_0=RT_s\ln[(\sqrt{2}\pi^{3/2}k^{5/2}/h^3)m_e(m_{Br_2})^{\frac{1}{2}}$$
$$\times(i_{Br_2}/i_e)(T_s^2T_r^{\frac{1}{2}}/P_{Br_2})(Q'_{Br}Q_e'/Q'_{Br})]. \tag{8}$$

The internal partition function Q' for electrons is 2. It is believed that no states of the bromide ion exist above the ground state, inasmuch as the nuclear shielding becomes practically complete when the electron is in a quantum state higher than the ground state. Consequently Q'_{Br^-} is set equal to one since the ground state is a singlet. The lowest term of the bromine atom $^2P_{3/2}$ has a degeneracy of 4 while the next member of the doublet lies 3685 cm^{-1} above the ground state. Thus we have

$$Q'_{Br}=4+2e^{-5300/T}. \tag{9}$$

The second term contributes, at the most, 0.05 kcal./mole to the electron affinity and hence this will be neglected.

Evaluating the constants in Eq. (8) one obtains for the working equation with ΔE_0 in kilocalories per mole and P_{Br_2} expressed in microns,

$$-\Delta E_0=4.575\frac{T_s}{1000}\left(\log 100\frac{i_{Br^-}}{i_e}-\log P_{Br_2}\right.$$
$$\left.+2\log\frac{T_s}{1000}+7.964\right). \tag{10}$$

DESCRIPTION OF APPARATUS

The central part of the apparatus, the reaction tube, was constructed along lines similar to that described previously.[2] This is shown schematically in Fig. 1. The filament F is suspended vertically by means of a tungsten spring so that it is kept taut when heated electrically. This is closely surrounded by a radial grid G and the latter by cylindrical plates and guard rings P and R. These are fixed in a Pyrex tube, and the whole surrounded on the outside by the solenoid S, coaxial with F. By means of a suitable electrical system, G and P and R may be maintained at the potentials V_G and V_P, respectively, with V_P, V_G, V_F. The flow of current to the plate may then be determined by means of the galvanometer connected in series with P.

When the tube is filled with the bromine, streaming through at constant pressure, and the filament heated to a known temperature, ions and electrons will travel radially to the plate, giving a galvanometer deflection. If a current is passed through the solenoid, the electrons will be deflected into the grid, while there will be no appreciable effect on the current to the plate due to the heavy ions. Therefore the galvanometer deflections due to ions i_i and to electrons i_e may be determined independently under fixed conditions of P_{Br_2} and T_s.

The reaction tube used here differed from the

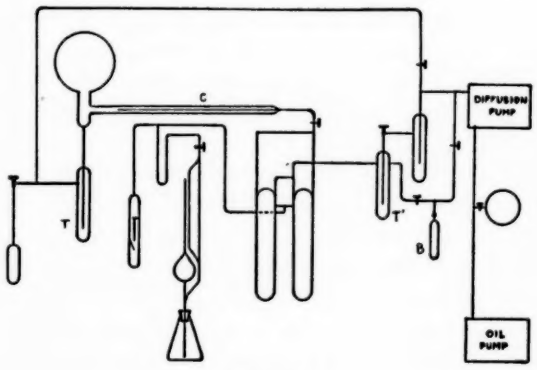

FIG. 2.

one described[2] in that a large ground glass joint (lubricated with graphite and Apiezon L) replaced the glass seal in joining the filament and grid support to the reaction tube. Furthermore, a longer filament (11.34 cm) was used and this was soldered directly to the supports.

A control tube, similar to the reaction tube but without grid, plate, and guard rings, was mounted in series with the reaction tube. This control tube was not necessary for the actual measurements but was used for the measurement of heat loss of the wire described later.

The diagram (Fig. 2) of the vacuum system shows how bromine is permitted to leak through the capillary C at a rate determined by the temperature of the trap T. After flowing through the tubes it is frozen out in trap T' which is cooled in liquid nitrogen. At the end of the run the bromine is removed by distilling into the bulb B which can be detached and emptied without breaking the vacuum in the system.

The pressure is measured with a quartz fiber gauge. The decay of the fiber oscillations is observed by light reflected into a telescope with a graduated eyepiece. The gauge is surrounded by mineral oil to prevent external vibrations from reaching the fiber.

In order to make measurements at lower filament temperatures a FP-54 amplifier was constructed and the input connected to the plate of the reaction tube. This enabled one to measure plate current with a sensitivity of 1×10^{-14} amp./mm.

THE ATTAINMENT OF THERMAL EQUILIBRIUM ON THE SURFACE

The assumption of unit accommodation coefficient which is necessary for the above derivation is supported by a large amount of evidence of an indirect nature.[2,3] Three additional points are offered below which indicate the correctness of this assumption.

(1) It has been shown recently[4] by calculations based on the data of Bryce[5] that the assumption is true for the case of hydrogen molecules and hot tungsten; i.e., all the hydrogen molecules hitting a hot tungsten filament come to equilibrium concentrations determined by the temperature of the filament and the number of molecules striking. It is quite reasonable then that the

[2] K. J. McCallum and J. E. Mayer, J. Chem. Phys. **11**, 55 (1943).

[3] H. B. Weisblatt, Dissertation, Johns Hopkins University, 1938.

[4] P. M. Doty, J. Chem. Phys. **11**, 557 (1943).

[5] G. Bryce, Proc. Camb. Phil. Soc. **32**, 648 (1936).

same situation may exist for the halogens and tungsten.

(2) In this investigation measurements of the electron affinity have been made over a range of 80-fold in pressure and 700° in temperature. No change or trend in the calculated value of the electron affinity could be detected. Since a change of accommodation coefficient is equivalent to a corresponding change in pressure, our data show that over the ranges covered by the experiment the accommodation coefficient could not have changed more than 10 percent. It seems reasonable to explain a constant accommodation coefficient by a value of unity.

(3) If all the bromine molecules which collide with the hot filament decompose, the filament should lose energy by an amount equal to the heat of dissociation of the molecules hitting plus the energy given to the atoms formed. Now the energy loss to the filament may be found by measurements of the current passing through the filament and the voltage across the filament, first for a vacuum and then for a given pressure of bromine. From these one may calculate the watts w used and the resistance R of the filament. Using this information one may then determine the energy loss D of the filament due to the bromine by means of the equation:

$$D=(W_{\text{vac}}-W_{\text{Br}_2})-[(dW/dT)/(dR/dT)]\times(R_{\text{vac}}-R_{\text{Br}_2}). \quad (11)$$

This has been done at a pressure of 21 microns at various temperatures. In Table I are recorded the temperatures (from the resistance function) together with the observed energy loss per mole of bromine and the theoretical energy loss (calculated on the basis of a unit accommodation coefficient) which is the energy E of dissociation at room temperature T_r, plus $3R(T_f-T_r)$ for the energy given to the two moles of bromine atoms formed. This table shows that the energy loss of the filament corresponds within experimental error ($\sim$15 percent) to the energy loss that would occur if the accommodation coefficient were unity. The energy loss differs from that calculated in the direction that is impossible according to the laws of thermodynamics. We may say that these experiments show the existence of unit accommodation coefficient. Similar calculations on data obtained during the measurements yield results which are similar but less accurate because at the lower pressures the effect was smaller. The objection may be raised that the presence of some bromine on the surface may increase the emissivity of the filament. However, this effect is not likely to be appreciable inasmuch as the heat loss measurements show no trend and since the amount of bromine present at any instant is probably much less than a monoatomic layer.

TABLE I. Energy loss of tungsten filament surrounded by bromine.

Temp. (Vac.) °K	Temp. (Bromine) °K	Observed energy loss kcal./mole	$E+3R(T_f-T_r)$ kcal./mole
2021	1987	62	55.5
1798	1753	62	54.5
1622	1560	54	52.1

MEASUREMENTS

The values of the electron affinity calculated from the measurements in this investigation show a dispersion which is less than that of other investigations[1,2] by at least a factor of two. It is believed that this increased precision is largely due to the use of an improved technique of obtaining filament temperatures.

The filaments were aged by suspending a loop of tungsten wire (25 cm), held taut by a weight, in a vacuum. After being heated to 2800°K for 15 minutes two straight pieces were cut from the loop. The diameter was determined to 0.01 percent by weighing and measuring the lengths with a cathetometer. These filaments were mounted in the control and reaction tubes which were then baked out in a vacuum overnight (450°C).

Measurements of current and voltage were made immediately after passing sufficient current through the two filaments in series to bring them to a moderate temperature (about 2000°K). It was observed that the resistance and wattage agreed accurately with those of a filament of the known diameter tabulated by Jones and Langmuir.[6]

During the runs the diameter alters with time, but by measuring watts *versus* resistance in vacuum several times during the run the diam-

[6] H. A. Jones and I. Langmuir, Gen. Elec. Rev. **419**, 310 (1927).

eter may be determined accurately for that run. That the procedure was correct could be checked by observing that with this calculated diameter the temperatures obtained from the watts, and from the resistances agreed to within two degrees at all temperatures. The resistance function was used to obtain the temperature when bromine was present.

The bromine (Mallinckrodt N.F.) was distilled several times in vacuum, the first portion of the distillate being discarded each time. This was done in order to eliminate chlorine and fluorine, the only impurities that would introduce an error greater than their effect on the pressure determination. The maximum amount of chlorine present in the undistilled bromine was 0.3 percent. Assuming all this remained after distillation the electron affinity here obtained would be 0.04 kcal. too large.

The silver parts of the reaction tube (grid, plate, and guard rings) were coated with silver chloride to prevent reaction with bromine.

In a typical run the grid potential would be set at 3 volts and the plate and guard rings at 6 volts positive with respect to the positive and of the filament, i.e., the end which is not grounded. After voltage and current measurements were made in a vacuum, bromine was allowed to flow through the system at a constant rate. Voltage and current measurements were repeated with the filament at a steady temperature and the pressure and galvanometer deflections (with and without solenoid current on) were recorded. Frequently the effect of solenoid current would be checked and any value between 3 and 6 amperes was found to be satisfactory. For each calculation of electron affinity several measurements of pressure, filament current and voltage, and plate current were made. When the amplifier was used (below 1850°K) the measurements of plate current with and without solenoid were made using the same grid leak in the amplifier in order to avoid errors that might arise from the relative calibration of two leaks.

TABLE II. Electron affinity of bromine.

Pressure (microns)	Temp. °K	$100(i_{Br^-}/i_+)$	$-\Delta E_0$	Deviation
21.2	1966	53.9	80.62	+0.13
17.2	2180	4.25	80.21	−0.28
9.50	2276	0.883	79.87	−0.62
6.90	1929	25.6	80.35	−0.14
6.80	1878	52.8	80.78	+0.29
5.40	2048	5.13	80.26	−0.23
4.85	2110	2.24	79.90	−0.59
3.50	1893	20.6	80.45	−0.04
2.60	1943	8.1	80.29	−0.20
2.00	2034	2.36	80.51	+0.02
1.85	2217	0.377	80.92	+0.43
1.74	2106	1.09	80.98	+0.49
1.72	2143	0.775	81.11	+0.62
5.00	1823	91.0	81.02	+0.53
1.43	1678	118.	79.99	−0.50
1.10	1679	125.	80.44	−0.05
0.88	1607	263.	79.78	−0.71
0.39	1610	172.	81.29	+0.60
		Average	80.49	0.36

TABLE III.

Investigator	Reference	Value kcal./mole	Method
Ionov	a	83.9	Ratio of + to − ions on hot tunsten hit by beam of KBr
Weisblatt, Mayer	b	80.0	Similar to this but with less accuracy
Van Arkel, de Boer	c	87.6	Only two temperatures Born cycles
Mayer and Helmholtz	d	81.5	Born cycles
Verwey and de Boer	e	77.2	Born cycles
Huggins, Rice	f	81.8	Born cycles
Glockler, Calvin	g	88.	Experimental (space charge)
Mayer and Helhmoltz	h	88.3	Dissociation of alkali halides
Saha and Tandon	i	80.0	Dissociation of alkali halides
Blewett	j	87.	Mass spectrograph
Lederle	k	82.	Absorption spectra
This experiment		80.5±0.4	

[a] N. I. Ionov, Comptes rendus Acad. Sci. U.S.S.R. **28**, 512 (1940).
[b] See reference 3.
[c] A. E. Van Arkel and J. H. De Boer, Physica **7**, 12 (1927).
[d] J. E. Mayer and L. Helmholtz, Zeits. f. Physik **75**, 19 (1932).
[e] E. J. W. Verwey and J. H. De Boer, Rec. trav. chim. **55**, 431 (1936).
[f] M. L. Huggins, J. Chem. Phys. **5**, 143 (1937).
[g] G. Glockler and M. E. Calvin, J. Chem. Phys. **3**, 771 (1935).
[h] L. Helmholtz and J. E. Mayer, J. Chem. Phys. **2**, 245 (1934).
[i] N. K. Saha and A. N. Tandon, Proc. Nat. Inst. Sci. Ind. **3**, 387 (1937).
[j] J. P. Blewett, Phys. Rev. **49**, 900 (1936).
[k] E. Lederle, Zeits. f. Physik **7**, 328 (1933).

RESULTS

In Table II are listed the results of this investigation. The pressure, temperature, and ratio of ions to electrons are given together with the electron affinity calculated from Eq. (10) and the deviations from the mean. Every measure-

ment made after the preliminary work was finished is included in Table II. These measurements extend from 1607° to 2276°K and from 0.39 to 21.2 microns pressure of bromine. The measurements could have been extended somewhat beyond this range, but with increasing difficulty. At higher temperatures (when the electron current exceeds 10^{-3}) the plate current becomes space charge controlled. At temperatures lower than 1600° pressures too low for accurate measurement on the quartz fiber gauge are necessary. The last five measurements in Table II were obtained with the aid of the amplifier.

The assignment of a precision measure to the value of the electron affinity is found by taking the square root of the sum of the squares of the deviation of the mean and the residual errors. The deviation of the mean (A.D.) is ± 0.08. The residual error in the temperature measurements is estimated to be 5° (0.25 percent), in the pressure 8 percent, in the ion-electron ratio 5 percent; these correspond respectively to errors of 0.2, 0.3, and 0.2 kcal./mole in the calculated electron affinity. In this manner one arrives at a precision measure of ± 0.42. Thus, the electron affinity of bromine is found to be 80.5 ± 0.4 kcal./mole.

Several other investigations of the electron affinity of bromine are summarized in Table III.

DISCUSSION

Another observation may be made from the constancy of the calculated values of the electron affinity presented in Table II. This constancy shows the correctness of the assumption made at the beginning requiring the pressure of bromine atoms leaving the surface to equal twice the pressure of bromine molecules in the gas phase. This corresponds precisely to the definition of a first-order reaction. Hence the decomposition of bromine on tungsten above 1600°K and below 22 microns pressure is a first-order reaction with an activation energy equal to the energy of decomposition. This may be compared with the first-order decomposition of hydrogen iodide on platinum[7] and of nitrous oxide on gold.[8] On the other hand, the high temperature decompositions of ammonia on tungsten[9] and hydrogen iodide on gold[10] are zero-order reactions.

[7] C. N. Hinshelwood and R. E. Burk, J. Chem. Soc. **127**, 2896 (1925).
[8] C. N. Hinshelwood and C. R. Prichard, Proc. Roy. Soc. **A108**, 211 (1929).
[9] C. H. Kunsman, E. S. Lamar, and W. E. Deming, Phil. Mag. **10**, 1015 (1930).
[10] C. N. Hinshelwood and C. R. Prichard, J. Chem. Soc. **127**, 1552 (1925).

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The Spectrum of Deuteroacetone in the Vacuum Ultraviolet

A Comparison with the Spectrum of Acetone

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The spectrum of acetone-d_6 of over 90 percent purity has been photographed in the region 2000–1300A, with a dispersion of 4.14A per mm. Data for the transition at about 51,000 cm^{-1} are presented together with new data on acetone in the same region. A discussion of the normal state of the acetones is given, and an analysis is made of the electronic spectra. It is shown that no vibrational frequency near 1200 cm^{-1} appears in the excited state of acetone-d_6 and that this frequency in acetone cannot be ascribed to the C–O vibration.

THE spectrum of acetone[1] and other simple ketones[2] consists of relatively sharp bands in the region 51,000–54,000 cm^{-1}. In all attempted analyses of these spectra there has been found a frequency in the neighborhood of 1200 cm^{-1} which has been ascribed to the C–O vibration. It is well known that this frequency has a value of about 1700 cm^{-1} in the normal states of compounds which contain this group. The electronic spectrum of deuteroformaldehyde[3] in the region 30,000 cm^{-1} has revealed also the presence of the 1200-cm^{-1} frequency which must be interpreted as the carbonyl frequency in this case.

We have prepared samples of almost pure acetone-d_6. Over 90 percent of the hydrogen has been replaced by deuterium as shown by analysis and by the relative simplicity of the spectrum. The spectrum of these samples has been examined in the 50,000-cm^{-1} region in an attempt to find this 1200-cm^{-1} carbonyl frequency. Such a frequency is shown definitely to be absent. The interpretation of such a frequency in acetone (and presumably in other ketones in this region) as the C–O frequency therefore becomes untenable, since the electronic transitions are surely the same. In the subsequent discussion an alternate interpretation will be given.

EXPERIMENTAL

The deuteroacetone was prepared by repeated exchange of acetone (Merck reagent, aldehyde free) with 99.6 percent D_2O using NaOD as catalyst.[4] After separation from most of the water by distillation in a vacuum through anhydrous calcium chloride, it was dried with anhydrous $CuSO_2$ and purified by vacuum distillation. A small sample was burned to water and analyzed for D content by the thermal conductivity method.[5] A sample showing over 90 percent D content could be produced after four exchanges.

The plates were taken with a normal incidence vacuum spectrograph[2] containing a 2-meter radius 120,000-line grating. The light source was a conventional hydrogen discharge operated at 3–4 kilowatts. Exposure times were 20 minutes with Eastman 103a–0 ultraviolet sensitized plates. The deuteroacetone vapor was introduced through calibrated volumes directly into the spectrograph which was shut off from the pumps during exposures. It was estimated that the pressures of deuteroacetone in the spectrograph were from 0.005 to 0.07 mm on the assumption that the vapor pressures of acetone and deuteroacetone are the same at 0°C. Most plates of acetone were taken in a pressure range of 0.005 to 0.04 mm. A few plates of acetone were taken at high pressures (5–20 mm) in the spectrograph to give the lowest frequency bands. Since we did

* Part of a dissertation presented to the Faculty of the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] W. Albert Noyes, Jr., A. B. F. Duncan, and Winston M. Manning, J. Chem. Phys. **2**, 717 (1934).

[2] A. B. F. Duncan, J. Chem. Phys. **8**, 444 (1940).

[3] E. H. Ebers, Ph.D. Thesis (Harvard University, 1935).

[4] (a) O. Reitz, Zeits. f. physik. Chemie **A179**, 119 (1937). (b) W. D. Walters and K. F. Bonhoeffer, Zeits. f. physik. Chemie **A182**, 265 (1938).

[5] P. Harteck, Zeits. f. Electrochemie **44**, 3 (1938).

not have enough deuteroacetone to fill the spectrograph (volume about 225 liters) at such high pressures, a quartz cell 20 cm long was introduced between the source and the slit and correspondingly higher pressures (up to 70 mm) of deuteroacetone used to bring out the low frequency bands. The absorbing column was at room temperature.

Most of the plates were measured with a precision comparator using the following reference lines:[6]

C I 1930.930,
N I 1745.250,
N I 1742.734.

The error in measurement of sharp bands in this way probably does not exceed 2–3 cm^{-1}. The dispersion was about 4.14A per mm.

The bands appearing only at very high pressures could not be measured in this way because these standard lines were absorbed, and no additional standard lines were present in this region. Recourse had to be made to a rather crude method of measurement from enlarged reproductions of these spectra, utilizing standard lines in adjacent spectra. The error in these measurements is therefore higher but still less than 7 cm^{-1} as judged from measurements of many different plates.

The experimental results of the electronic spectra are given in Table II, but before discussion of this table the normal state of acetone and deuteroacetone will be considered.

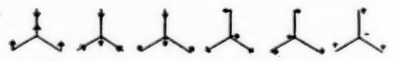
NORMAL STATE

Analysis of the spectra of acetone and deuteroacetone must start with a discussion of the symmetry properties of the molecules and their normal vibrations. A general treatment requires no symmetry (C_1), although C_{2v} symmetry is possible for a rigid and symmetrical arrangement of the methyl groups relative to one plane through the C−O group.

However, if we treat the methyl groups as points, or assume that the groups rotate freely, the model certainly corresponds to symmetry C_{2v} and the discussion appears to be profitable. This may be justified if the force constants which determine the internal hydrogen frequencies do not affect appreciably the vibrations of the Me_2CO framework. There will be six frequencies belonging to this four-atom model which have symmetries A_1 (3), B_1 (2), B_2 (1). All six frequencies are permitted in the Raman effect and in the infra-red spectra. In the Raman effect the three frequencies of representation A_1 should have low depolarization ratios and the other three should have depolarization ratios of $\frac{6}{7}$ for light initially unpolarized.

The Raman spectrum of deuteroacetone was investigated by Engler,[7] but depolarization

TABLE I. Forms of vibration and Raman frequencies of acetone and deuteroacetone.

Form of vibration (after Wu)[a]							
Notations							
Present	ω_3	ω_1	ω_2	ω_4	ω_5	ω_6	ω_H
Engler,[b] Kohlrausch and Pongratz[c]	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_2'
Aston and Schumann[d]	$\nu_2(\pi)$	$\nu_1(\pi)$	$\delta(\pi)$	$\nu_1(\sigma)$	$\delta_1(\sigma)$	$\delta_2(\sigma)$	$^2\delta(\pi)$
Symmetry	A_1	A_1	A_1	B_1	B_1	B_2	A_1
Present assignment of acetone frequencies from data of reference e	1710	1066	787	530	488	391	1356
Present assignment of acetone-d_6 frequencies from Engler's data	1710	895	700	483	413	335	1093
Depolarization ratios (acetone)							
Reference e	0.38	0.64	0.20	0.70	0.90	0.87	0.60
Edsall and Wilson[f]	*P*	*P*	*P*	*D*	*D*	*D*	*P*
Other assignments of acetone frequencies							
Kohlrausch and Pongratz	1710	787	530	1066	391*	391*	1356
Engler	1710	787	530	1066	391	—	1356
Aston and Schumann	1710	787	391	1066	530	530	1220
Acetone-d_6 frequencies							
Engler's assignment	1710	700	483	1038	335	—	1038
Teller product							
(calc.)		1.27		1.16		1.02	
(obs.)		1.34		1.31		1.17	

[a] T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Prentice-Hall, Inc., New York, 1940), p. 208.
[b] See reference 7.
[c] See reference 10.
[d] See reference 13.
[e] See reference 8.
[f] See reference 11.
* Kohlrausch and Pongratz were uncertain whether to assign 391 to ω_5 or ω_6.

[6] J. C. Boyce and J. T. Moore, *Provisional Wavelength Identification Tables for the Vacuum Ultraviolet* (1941).

[7] W. Engler, Zeits. f. physik. Chemie **B35**, 433 (1937).

ratios were not obtained. The Raman spectrum of acetone has been obtained by many workers[8] and depolarization data are available. The infrared spectrum of acetone vapor has been studied.[9] Previous attempts at analysis have been made, and their conclusions relative to the Me_2CO frequencies for acetone and deuteroacetone together with the present assignment are shown in Table I. It should be pointed out that the wide divergencies in assignment are due either to ignorance of the data on depolarization of Raman lines or in interpretation of the depolarization data themselves. For example, the 1066-cm^{-1} line was considered depolarized by Kohlrausch and Pongratz[10] and by Engler. More recent work of Edsall and Wilson[11] (especially their Fig. 4) shows that it must be polarized, which agrees with the earlier work of Simons.[12] The 530-cm^{-1} line has a depolarization ratio of 0.70, and this has been interpreted as indicating that the line is polarized by Kohlrausch and Pongratz and by Engler; but Edsall and Wilson show that this line is depolarized. Kohlrausch and Pongratz inconclusively assign 391 cm^{-1} to ω_5 or ω_6, and Engler assigns this to ω_5.

Our present assignment is based on the following reasoning. The depolarization data show rather unambiguously that the A_1 frequencies are 1710, 1066, and 787, and the B frequencies are 530, 488, and 391.[13] The vibration ω_6 of symmetry B_2 should have the lowest frequency so it is assigned the value 391. The 1710-cm^{-1} vibration of A_1 may be assigned to the model unambiguously. 1066 and 787 of A_1 and 530 and 488 of B_1 are assigned arbitrarily to stretching and bending, respectively, because stretching frequencies usually appear to be larger. This is, however, of no importance to our discussion.

Our assignments of the deuteroacetone lines differ from Engler for the following reasons. Our reassignment of 530 and 488 to B_1 in acetone will automatically change Engler's assignments to agree with ours in this respect since he has correlated 483 and 413 in deuteroacetone with the above acetone values. Our choice of the correspondence of 1066 with 895 in acetone and deuteroacetone rather than the correspondence of 1066 with 1038 proposed by Engler arises from this consideration. In the electronic spectra, to be discussed later, very few bands arising from vibrational levels of the ground state are found. In acetone these show frequency differences of 1066 and 1357 in acetone, and 895 and 1087 in deuteroacetone. From similarity of appearance, pressure dependence at constant temperature, and temperature dependence, 1066 definitely corresponds to 895 and 1357 to 1087, in acetone and deuteroacetone, respectively. The frequencies 1357 and 1087 in the two molecules are assigned to symmetrical hydrogen bending and designated as ω_H in Table I. The other symmetrical hydrogen frequency (stretching) is not necessary to our discussion.

Some confirmation of the above assignments may be found in the calculated and observed values of the Teller (or Redlich) isotope product ratios[14] shown in Table I. On the simple assumption that the force constants are unchanged, poor agreement with experiment was obtained. This is to be expected since in the C_{2v} model we are substituting CH_3 by CD_3 and not H by D. To refine these calculations, we may make assumptions regarding the change of force constants with distance in the two molecules since the CH_3 and CD_3 groups are considered as units. It may be assumed that the masses of CH_3 and CD_3 act at their respective centers of gravity and the C−H and C−D distances are not changed. In this case the C−C distance must be different in the two molecules; or if the C−C distance is to remain fixed, different effective masses for CH_3 and CD_3 must be used giving the

[8] F. F. Cleveland, M. J. Murray, J. R. Coley, and V. I. Komarewsky, J. Chem. Phys. **10**, 18 (1942).

[9] (a) Donna Price, J. Chem. Phys. **9**, 725 (1941). (b) W. W. Coblentz, *Investigations of Infra-Red Spectra. Part I* (Carnegie Institution Publication, 1905).

[10] K. W. F. Kohlrausch and A. Pongratz, Zeits. f. physik. Chemie **B27**, 180 (1934).

[11] J. T. Edsall and E. B. Wilson, J. Chem. Phys. **6**, 124 (1938).

[12] L. Simons, Soc. Sci. Fenn. Com. Phys. Math. **6**, No. 13 (1932).

[13] There are two low frequency lines 587 and 731 cm^{-1} of very low intensity and unknown depolarization which do not fall into any assignment. Lines corresponding to these do not appear in the Raman spectrum of deuteroacetone. The acetone frequency 901 cm^{-1} appears strongly in the infra-red (880 cm^{-1}) and may be associated with internal rotation [cf. S. C. Schumann and J. G. Aston, J. Chem. Phys. **6**, 485 (1938).]

[14] (a) W. R. Angus, C. R. Bailey, J. B. Hale, C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson, and C. L. Wilson, J. Chem. Soc., p. 971 (1936). (b) O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935).

TABLE II. Wave numbers of bands in acetone and acetone-d_6.

Transitions $\nu=\nu_0+\omega_i'$

Acetone

	ω_6'		ω_5'		ω_2'		ω_1'		ω_H'	
51181	(269)	51450	(315)	51496	(714)	51895	(1047)	52228	(1194)	52375
51199	(276)	51475	(327)	51526	(715)	51914	(1049)	52248	(1194)	52393
51227			(328)	51555	(716)	51943			(1192)	52419
51241										
51253			(326)	51579	(714)	51967	(1042)	52295	(1190)	52443
51287					(723)	52010	(1036)	52323	(1190)	52477
51313					(742)	52055	(1038)	52351	(1200)	52513
51350					(724)	52074			(1186)	52536

Acetone-d_6

	ω_6'		ω_5'		ω_2'		ω_1'		ω_H'	
51302	(237)	51539	(259)	51561	(612)	51914	(816)	52118	(906)	52208
51317			(266)	51583	(615)	51932	(821)	52138	(906)	52223
51333			(273)	51606	(614)	51947	(816)	52149	(908)	52241
								52162		
51354			(273)	51627	(615)	51969	(819)	52173	(907)	52261
51374					(610)	51984	(820)	52194	(912)	52286
51390					(614)	52004			(910)	52300
51421									(913)	52334
51460									(912)	52372
51511										

Transitions $\nu=\nu_0+2\omega_i'$

Acetone

ω_1'	ω_1'	
(1047+1041)		53269
(1049+1042)		53290
(1042+1041)		53336
(1036+1044)		53367

Acetone-d_6

ω_1'	ω_1'	
(816+819)		52937
(821+814)		52952
(816+819)		52968
(819+814)		52987

Transitions $\nu=\nu_0+\omega_H'+\omega_1'$

Acetone

ω_H'	ω_1'	
(1194+1041)		53416
(1194+1041)		53434
(1190+1027)		53470
(1190+1026)		53503
(1186+1021)		53557

Acetone-d_6

ω_H'	ω_1'	
(906+815)		53029
(906+817)		53040
(908+814)		53055
(910+806)		53106
(912+792)		53164

Transitions $\nu=\nu_0-\omega_i''$

Acetone

	ω_1''		ω_H''	
51181	(1062)	50119	(1352)	49829
51199	(1063)	50136	(1357)	49842
51227	(1064)	50163	(1356)	49873
51253	(1070)	50183	(1358)	49895
51287	(1070)	50217		

Acetone-d_6

	ω_1''		ω_H''	
51302	(883)	50419	(1085)	50217
51317	(884)	50433	(1087)	50230
51333	(881)	50452	(1089)	50244
51354	(883)	50471	(1083)	50271

Transitions $\nu=\nu_0+\omega_5'-\omega_5''$

Acetone

ω_5'	ω_5''	
(315−487)		51009
(327−503)		51023
(328−500)		51055
(326−503)		51076

Acetone-d_6

ω_5'	ω_5''	
(259−404)		51158
(266−408)		51175
(273−410)		51196
(273−414)		51213
		51234

same result. We have assumed that only one (stretching) constant changes, which affects only the products for A_1 and B_1. The value for A_1 is brought into what is probably satisfactory agreement. The change of the constant with distance was calculated from the rules of Badger[15] and Clark[16] which gave identical results. The residual lack of agreement in the isotope product ratios is ascribed to neglect of the numerous

[15] R. M. Badger, J. Chem. Phys. **2**, 128 (1934).
[16] C. H. Douglas-Clark, Trans. Faraday Soc. **31**, 1017 (1935).

possible interaction constants[17] in the potential energy, whose magnitudes must mostly be guessed. These are constants not only pertinent to the model C_{2v} being discussed but also those for interaction between motions of the methyl groups with the rest of the molecule.[18] These interaction constants should affect particularly the B_1 and B_2 ratios. It may be pointed out, however, that any change in our assignment of B_1 and B_2 frequencies makes the products generally worse.

ELECTRONIC TRANSITION

Table II shows measurement of acetone and deuteroacetone in the region 40,000–60,000 cm^{-1} from recent plates. Figure 1 shows key transitions in an energy level diagram. Figure 2 shows a few microphotometer traces from representative plates. The data are arranged in Table II so that with these figures the analysis and discussion will be clear. To avoid confusion the frequencies of acetone bands only are used in the following discussion. Corresponding deuteroacetone bands may be easily found from Table II.

The positions of all bands are expressed by an equation $\nu=\nu_0+\sum n\omega_i'-\omega_i''$ where ν is the frequency in cm^{-1} of the transition, ν_0 the frequency of the electronic transition between non-vibrating

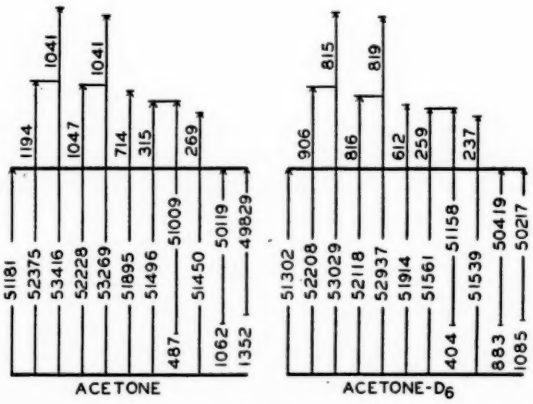


FIG. 1. Key transitions in acetone and acetone-d_6.

states, ω_i'' and ω_i' are vibration frequencies of the normal and excited states of the molecule,

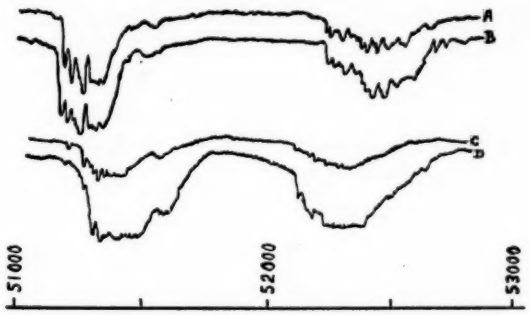


FIG. 2. Microphotometer traces of typical plates. *A*, acetone, 0.005-mm pressure. *B*, acetone, 0.01-mm pressure. *C*, acetone-d_6, 0.01-mm pressure. *D*, acetone-d_6, 0.02-mm pressure.

respectively, and n the number of quanta of vibration ω_i' excited. Most transitions are seen to be of the simple type $\nu=\nu_0+\omega_i'$ where one quantum of vibration is added to the electronic transition. There are a few cases in which more than one quantum of vibration is added but no long progressions. The notation used in regard to i in ω_i may appear arbitrary, but we followed the conventions of others where any consistency exists. In any case, the notation will be apparent from Table I.

Most of the bands consist of numerous groups of sub-bands, possibly due to the unresolved rotational structure. The total width of the bands is quite consistent with reasonable values of the moment of inertia. For example, ν_0 itself consists of 6 and possibly 8 sub-bands, of which 51, 181, 51,199, and 51,253 appear to be most important. In Fig. 1 this appears as a single transition 51,181. Other transitions $\nu_0+\omega_i$, etc., also consist of such sub-bands which show striking similarities both in visual examination of plates and differences from the ν_0 sub-bands. Corresponding sub-bands appear in the same row in the table. The values of ω_i are given in parentheses for corresponding sub-bands. The absolute values of ω_i' obtained in this way are probably not too significant. Since we have not attempted to interpret the sub-bands and there appears little hope of doing this, we have rather arbitrarily chosen to take differences from sub-bands which appeared to be similar.

Since all measurements are made from ν_0 (51,181 cm^{-1}), the choice of this as the origin of the electronic transition may be questioned. This

[17] B. L. Crawford, Jr., and S. R. Brinkley, Jr., J. Chem. Phys. **9**, 69 (1941).
[18] O. Redlich and L. E. Neilson, J. Am. Chem. Soc. **65**, 654 (1943).

band has the highest intensity of the whole transition. (Actually a sub-band 51,253 of ν_0 is more intense, but this does not affect our frequency differences since the corresponding sub-band is always most intense in other bands.) No other bands appear to the red until the temperature or pressure is greatly increased, and when this is done, the only bands appearing are separated from ν_0 by normal state frequencies. These facts all point to an allowed electronic transition with the above origin. If a forbidden electronic transition were present instead, it would be allowed by a vibration B_1 or B_2 excited in either the normal or excited state. The existence of two high temperature bands separated from our chosen ν_0 by exact normal state frequencies gives the most positive evidence against 51,181 cm^{-1} being a transition $\nu_0+\omega_B'$, where ω_B' is the vibration excited in the upper state which allows the forbidden transition. If this were so, then it would be necessary that the frequencies obtained from the high temperature bands must be diminished by ω_B' (of symmetry B_1 or B_2) and still give other normal state frequencies. This may be tested since we have the two observed frequencies. It follows that $\omega_H''-\omega_1''$ must be the exact difference of two other normal state frequencies $\omega_x''-\omega_y''$ and that $(\omega_H''+\omega_1'')-(\omega_x''+\omega_y'')=2\omega_B'$. Now ω_B' must be less than ω_B''. Substitution of all known values of ω_x'' and ω_y'' gives values of ω_B' greater than any known ω_B''. It must be further pointed out that the experimental value of the intensity of the whole electronic transition[19] determined in solution and the theoretical calculations[20] indicated that the transition is allowed. Exactly the same conclusion may be drawn in regard to the transition in deuteroacetone.

If ν_0 has been correctly assigned on the basis of these considerations, the interpretation of the other excited state frequencies requires little comment. The most obvious frequency difference in acetone is 1194. Even visual examination shows that this frequency is absent in deuteroacetone. Addition of this frequency to ν_0 (51,302) brings us to a region of relatively high transmission. We must conclude, therefore, that 1194 cm^{-1} in acetone cannot be assigned to the C−O frequency. The corresponding frequency of equal prominence which we do find in deuteroacetone is 906 cm^{-1}. It is concluded that 1194 cm^{-1} in acetone and 906 in deuteroacetone are due to hydrogen bending in the methyl groups which correspond to 1357 cm^{-1} and 1093 cm^{-1} of the normal states. It appears probable that the frequency of about 1200 cm^{-1} common to the excited states of ketones and aldehydes may be ascribed to hydrogen bending, except in the case of formaldehyde. In this case we cannot question its assignment to C−O stretching.

The correlation of the other normal and excited state frequencies which we have made will be apparent from Tables I and II. Of these the most prominent in the excited state is 1047, and it appears reasonable to assign it to a totally symmetrical vibration. It may be pointed out that this is the only frequency giving even a short progression. Of the remaining three excited state frequencies only 315 cm^{-1} requires additional comment, because of its connection with the transition $\nu=\nu_0+\omega_5'-\omega_5''$ at 51,009 cm^{-1}. The correlation of these three frequencies does not differ materially from previous suggestions of Noyes, Duncan, and Manning.

The band at 51,009 cm^{-1} in acetone is separated from ν_0 by only 172 cm^{-1}. Since we have not found independent evidence of a frequency of this magnitude in either the upper or lower state, the transition may arise from an excited level in the ground state and end on an excited level in the upper state. It appeared reasonable that the same vibration was concerned in both states. The difference between 51,009 cm^{-1} and ν_0 should then be equal to a difference $\omega_i''-\omega_i'$. The only known low normal frequency satisfying this condition is 488, which is 321 in the excited state. That the frequency must be a low one is shown from a qualitative study of the temperature dependence of the band. Support of this assignment is found in the spectrum of deuteroacetone where the corresponding band 51,158 cm^{-1} is separated from ν_0 by 144 cm^{-1}. This is approximately the difference $\omega_5''-\omega_5'$ for deuteroacetone.

A comparison of the present results with those obtained earlier by Noyes, Duncan, and Manning

[19] H. Ley and B. Arends, Zeits. f. physik. Chemie **B12**, 132 (1931).
[20] H. L. McMurray, J. Chem. Phys. **9**, 231 (1941).

in the same region apparently shows some inconsistencies which require comment at this point. The changes in numerical values of wave numbers of sub-bands are due partly to better resolution of the sub-bands and partly to changed values of reference lines. Disagreement with the former analysis is mainly in details concerning the sub-bands. A completely satisfactory analysis appears impossible without a quantitative interpretation of the sub-bands.

Our Table II, which we wished to represent the results of interpretation rather than a list of all transitions found, is incomplete in two respects. First, our data on deuteroacetone do not extend to frequencies as high as have been observed in acetone. Our data on acetone above 53,600 cm^{-1} are less complete than the former results of Noyes, Duncan, and Manning, though in no essential disagreement. We have accordingly omitted these from Table II. Second, we have omitted some transitions which appear at high pressures on the low frequency side of the main transitions in both acetones. We doubt whether these actually belong to the transitions they appear to precede, but a list of the bands is given and in parentheses following, the transition to which they may belong. In acetone we have found: 51,113 and perhaps others (ν_0); 52,168, 52,187, ($\nu_0+\omega_1'$); 62,114, 52,131 ($\nu_0+\omega_2'$); 53,068, 53,137 ($\nu_0+2\omega_1'$); 53,390 ($\nu_0+\omega_H'+\omega_1'$); 50,951 and others ($\nu_0+\omega_5'-\omega_5''$). In acetone-$d_6$ we have found: 51,265, 51,284, and perhaps others (ν_0); 52,029, 52,062 ($\nu_0+\omega_1'$); 52,881, 52,911 ($\nu_0+2\omega_1'$); 53,006 ($\nu_0+\omega_H'+\omega_1'$).

Our results on the spectrum of deuteroacetone at frequencies higher than 53,200 are incomplete. We were unable to find other bands belonging to this transition. We do find, however, the analog of the next electronic transition in acetone. In acetone this is at 60,079 and in deuteroacetone at 60,071. It is remarkable that there is so little difference in ν_0 values. The strongest transition in deuteroacetone is estimated to occur at a slightly higher frequency than in acetone (where it is at 65,218 cm^{-1}), but no measurement was made.

An Empirical Correlation and Method of Calculation of Barriers Hindering Internal Rotation

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The barriers hindering internal rotation of methyl groups can be calculated by assuming that they are solely due to repulsion between hydrogen atoms according to the law $V_{ij}=4.99\times10^5/r_{ij}^5$. For dimethyl ether, dimethyl sulfide, and propylene the empirically calculated values are low. This discrepancy is discussed. This treatment is applied to ethyl and isopropyl alcohol and several normal paraffins. The resulting entropies, heat capacities, and equilibrium constants are compared with the available experimental data.

I. INTRODUCTION

IN 1932 Eyring[1] calculated that a potential function of 360 calories hindered the mutual internal rotation of the methyl groups in ethane. Assuming this barrier Teller and Topley[2] made a calculation of the equilibrium constant for the hydrogenation of ethylene from the heat of hydrogenation and the spectroscopic and molecular data. They found a discrepancy which they pointed out would disappear if the barrier hindering internal rotation were actually 3000 calories instead of the 360 calculated by Eyring. A similar discrepancy per methyl group in tetramethyl methane[3] between the entropy calculated from spectroscopic and molecular data and that obtained using the third law of thermodynamics was wrongly interpreted as due to irregularities in the solid at low temperatures. Kemp, Pitzer, and Witt[4–6] measured the third law entropy of ethane, compared it with that calculated from spectroscopic data, and obtained a discrepancy of 1.6 e.u. They pointed out that a potential hindering the internal rotation of the methyl groups of 3150 calories in ethane and 4200 calories in tetramethylmethane[7] would explain all the existing facts. Since that time, the evidence for these large barriers has accumulated rapidly,[8] but an adequate explanation is still wanting. The most thorough investigation of possible causes of these barriers is that of Gorin, Walter, and Eyring.[9]

A summary of the measured values to date for the potential hindering the internal rotation of methyl groups in certain compounds is given in column three of Table I.

That the potential is due to repulsions is now generally agreed, the evidence being the decreasing barriers in going from tetramethyl methane[3,7] to tetramethyl silicon[10] and from dimethyl ether[11] to dimethyl sulfide[12] and the non-planarity of the cyclopentane ring.[13] In the present paper an empirical method is presented for calculating these potentials on the assumption that the barriers are due to repulsions involving hydrogen atoms only. This method is then applied to ethyl and isopropyl alcohol and normal paraffins.

II. GENERAL METHOD

With a force law for the repulsion between hydrogen atoms, the sum of all the terms due to the simultaneous interactions gives the potential for any arbitrary angular position of the rotating group. The difference between the maximum and

[1] H. Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).
[2] E. Teller and B. Topley, J. Chem. Soc., p. 876 (1935).
[3] J. G. Aston and G. H. Messerly, J. Am. Chem. Soc. **58**, 2354 (1936).
[4] J. D. Kemp and K. S. Pitzer, J. Chem. Phys. **4**, 749 (1936).
[5] R. K. Witt and J. D. Kemp, J. Am. Chem. Soc. **59**, 273 (1937).
[6] J. D. Kemp and K. S. Pitzer, J. Am. Chem. Soc. **59**, 276 (1937).
[7] K. S. Pitzer, J. Chem. Phys. **5**, 473 (1937).
[8] Cf. G. Glockler, Rev. Mod. Phys. **15**, 111 (1943).
[9] E. Gorin, J. Walter, and H. Eyring, J. Am. Chem. Soc. **61**, 1876 (1939).
[10] J. G. Aston, R. M. Kennedy, and G. H. Messerly, J. Am. Chem. Soc. **63**, 2343 (1941).
[11] R. M. Kennedy, M. L. Sagenkahn, and J. G. Aston, J. Am. Chem. Soc. **63**, 2267 (1941).
[12] D. W. Osborne, R. N. Doescher, and D. M. Yost, J. Chem. Phys. **8**, 506 (1940); J. Am. Chem. Soc. **64**, 169 (1942).
[13] J. G. Aston, S. C. Schumann, H. L. Fink, and P. M. Doty, J. Am. Chem. Soc. **63**, 2029 (1941); J. G. Aston, H. L. Fink, and S. C. Schumann, J. Am. Chem. Soc. **65**, 341 (1943).

TABLE I. Comparison of experimental and calculated potentials hindering rotation of methyl groups.

Compound	Molecular data	V (experimental)	V (calculated)
Ethane		3150[a] 2750[b]	3150
Propane	<CCC = 114°12′[c]	3300[d] 3400[e]	3170
Tetramethylmethane		4500[f,g]	4230
Tetramethylsilicon	C−Si = 1.93A[h]	1300[i]	1360
Dimethyl ether	<COC = 111°[j] C−O = 1.42A[j]	3100[k] 2500[l]	1600
Dimethyl sulfide	<CSC = 102°[h,m] C−S = 1.82A[h]	2000[m]	1260
Propylene	C=C = 1.36A	2120[n]	930
Methyl amine	<HNH = <CNH = 108°06′[h] N−H = 1.016A C−N = 1.47A	3000[o] 1520[p]	2925
Methyl alcohol	<COH = 105°[q] C−O = 1.42A[q] O−H = 0.96A[q]	3400[q]	2250
Methyl mercaptan	C−S = 1.83A S−H = 1.35A <CSH = 100°	1460[r]	860
Acetone		1000[s]	1390

[a] See references 4 and 6 of text.
[b] G. B. Kistiakowsky, J. R. Lacher, and F. Stitt, J. Chem. Phys. **7**, 289 (1939).
[c] S. H. Bauer, J. Chem. Phys. **4**, 406 (1936).
[d] J. D. Kemp and C. J. Egan, J. Am. Chem. Soc. **60**, 1521 (1938).
[e] G. B. Kistiakowsky, J. R. Lacher, and W. W. Ransom, J. Chem. Phys. **6**, 900 (1938).
[f] See references 3 and 7 of text.
[g] J. G. Aston, Chem. Rev. **27**, 59 (1940).
[h] L. O. Brockway and H. O. Jenkins, J. Am. Chem. Soc. **58**, 2036 (1936).
[i] See reference 10 of text.
[j] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **57**, 2684 (1935).
[k] See reference 11 of text.
[l] G. B. Kistiakowsky and W. W. Rice, J. Chem. Phys. **8**, 618 (1940).
[m] See reference 12 of text.
[n] B. L. Crawford, Jr., G. B. Kistiakowsky, W. W. Rice, A. J. Wells, and E. B. Wilson, Jr., J. Am. Chem. Soc. **61**, 2980 (1939).
[o] J. G. Aston, C. W. Siller, and G. H. Messerly, J. Am. Chem. Soc. **59**, 1743 (1937). A more accurate treatment by Pitzer's method using the frequencies in reference 19 also gives 3000 cal. for the barrier.
[p] J. G. Aston and P. M. Doty, J. Chem. Phys. **8**, 743 (1940).
[q] B. L. Crawford, Jr., J. Chem. Phys. **8**, 744 (1940).
[r] H. Russell, Jr., D. W. Osborne and D. M. Yost, J. Am. Chem. Soc. **64**, 165 (1942).
[s] S. C. Schumann and J. G. Aston, J. Chem. Phys. **6**, 485 (1938).

minimum of these sums gives a value for the potential barrier hindering the rotation of the group, if it be assumed that the potential function depends exclusively on hydrogen repulsions. It is simplest to take an expression for the potential of the form

$$V=\frac{k}{r_{ij}^{n}}, \tag{1}$$

where r_{ij} is the distance between a hydrogen atom i of the rotating group and a hydrogen atom j of the rest of the molecule which is being held stationary. The values of k and n are then obtained from the known potentials for ethane and tetramethyl methane. Insertion of these values in (1) gives

$$V=\frac{4.99\times10^{5}}{r_{ij}^{5}}, \tag{1a}$$

where the distance r_{ij} is expressed in angstrom units and the potential V is in calories per mole.

This expression allows the potential barriers to be calculated from the bond lengths and angles. The distance r_{ij} for various hydrogen pairs is expressed as a function of these and ϕ, the angular displacement of the rotating group from some reference position. At various assigned values of ϕ the different distances are evaluated and substituted in Eq. (1a). Thus,

$$V_{(\phi)}=4.99\times10^{5}\sum_{i,j}[1/r_{ij}(\phi)]^{5}. \tag{2}$$

The potential V is finally plotted against the displacement ϕ. The difference between a minimum and an adjacent maximum gives the potential barrier. In some cases mere examination of the tabulated values of V will indicate the location of the maxima and minima but in others a graph is necessary. In certain cases, the angles at which the maxima and minima are located are obvious and the calculation need be performed only at these angles. Different types of molecular models, e.g., Hirschfelder (as manufactured by the Fisher Scientific Company), have been found useful in studying the geometry of the different molecules. It should be noted, however, that at times inspection of these models may lead to conclusions that are erroneous and misleading.

In making the calculations for a single rotating group, a somewhat arbitrary but reasonable assumption has to be made about the position of the other groups in the molecule. It is assumed that all other groups remain in such a position that the potential between the parts of the molecule is at a minimum. The potential hindering rotation of any group in the molecule is thus determined by keeping all the others stationary.

Unfortunately in the case of some compounds there is uncertainty in the electron diffraction data which itself produces an uncertainty in the empirical calculation of the barrier far greater than in its experimental evaluation. The electron

diffraction data are less sensitive to changes in angles than this calculation of potential barriers, as will be seen in the case of dimethylether below.

In all cases the usual C−C and C−H distances, 1.54 and 1.09 angstrom units, respectively,[14] are used except where electron diffraction data definitely indicate other preferred values.

The expressions for the nine distances between hydrogen atom number 1 on the rotating methyl group and the nine others on the stationary groups in tetramethylmethane are as follows, where ϕ is zero for the position in which the C−H bonds lie in the planes bisecting the angles between the bonds joining the other methyl groups to the central atom.

$$r^2_{1,4} = 15.4571 + 2.9853 \cos\phi, \quad (3a)$$

$$r^2_{1,5} = 9.9289 + 4.0421 \cos\phi - 1.8298 \sin\phi, \quad (3b)$$

$$r^2_{1,6} = 9.9289 + 4.0421 \cos\phi + 1.8298 \sin\phi, \quad (3c)$$

$$r^2_{1,7} = 15.4559 - 1.4927 \cos\phi - 2.5844 \sin\phi, \quad (3d)$$

$$r^2_{1,8} = 9.9306 - 3.6062 \cos\phi - 2.5864 \sin\phi, \quad (3e)$$

$$r^2_{1,9} = 9.9304 - 0.4359 \cos\phi - 4.4163 \sin\phi, \quad (3f)$$

$$r^2_{1,10} = 15.4559 - 1.4927 \cos\phi + 2.5844 \sin\phi, \quad (3g)$$

$$r^2_{1,11} = 9.9304 - 0.4359 \cos\phi + 4.4163 \sin\phi, \quad (3h)$$

$$r^2_{1,12} = 9.9306 - 3.6062 \cos\phi + 2.5864 \sin\phi. \quad (3i)$$

For each of atoms 2 and 3 on the rotating group there are nine distances respectively equal to a corresponding one of those given above. Thus the potential due to all three hydrogens is three times that due to hydrogen atom number one. Use of Eq. (2) thus gives an expression which approximates very closely to

$$V = V_{\min} + V_0/2(1 - \cos 3\phi). \quad (4)$$

By similar calculations, Eyring[1] deduced the expression

$$d^2 = 7.53 - 2.27 \cos\phi \quad (5a)$$

for the distance d of a hydrogen on one methyl group in ethane from a hydrogen on the other. The corresponding expression used in the calculations of this paper is

$$d^2 = 7.2484 - 2.1136 \cos\phi. \quad (5b)$$

The smaller constants are due to our use of 1.09A for the C−H distance instead of 1.13A used by Eyring.

[14] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), second edition.

III. SIMPLE PARAFFINS

In this section the potential barriers hindering the internal rotation of methyl groups in certain simple hydrocarbons are calculated by the empirical method. The results are compared with the most recent experimental results in Table I.

The distances and angles used are given in the second column of the table. In all cases the C−H distance used was 1.09A and angles not given in column two were taken as tetrahedral.

The agreement for the paraffins, which make up the first four entries in Table I, is exceptionally good. The essential validity of this empirical method for compounds in which all the valence electrons are shared in single bonds seems established.

TABLE II. Calculation of hindering potentials considering the seat of repulsive force at covalent radius.

Compound	V (experimental)	V (calculated) $n=5$	V (calculated) $n=6$
Ethane	3150	3150	3150
Tetramethyl methane	4500	5920	4760
Tetramethyl silicon	1280	1410	920
k		7.84×10^5	1.16×10^6

Since there is no *a priori* reason for considering the centers of the repulsions to be on the hydrogen nuclei, it is desirable to study the effect of treating the centers elsewhere. For this reason, the calculations for the first three compounds were repeated with the centers of repulsion located at a point on the bond removed from the hydrogen nucleus by a distance equal to the covalent radius of the hydrogen atom, namely, 0.32A (the most probable position of the bonding electrons). The results obtained by these calculations are summarized in Table II. The calculations were performed with the power $n=5$ and $n=6$. In each case the constant k was adjusted to obtain the experimental value for ethane. This constant is listed in the last row of the table. With either integral power, the agreement is not quite as satisfactory as it was in the

previous calculation (see Table I). It does seem reasonable, however, to conclude that at least semi-quantitatively, conclusions obtained by considering the seat of the repulsions either at the hydrogen atoms or at the most probable position of the bonding electrons are substantially the same.

It has been assumed that there is no interaction due to the carbon atom in tetramethyl methane. A hydrogen atom on the rotating methyl group comes much closer to hydrogen atoms on the other methyl groups than it does to the carbon atoms of the other methyl groups. Thus it does not follow that there is any real difference between hydrogen hydrogen and hydrogen carbon interactions insofar as the force law is concerned.

It seems reasonable to believe that, whatever its meaning, calculation on the basis of Eq. (2), in most cases, should give a minimum value of the potential barrier hindering internal rotation of a group. As just mentioned no allowance is made for a repulsive effect of other atoms similar to that of hydrogen or due to permanent dipoles; nor is any allowance made for "steric" effects in the usual sense of the term. Occasionally these effects may reduce the barriers by tending to equalize the potential field but more usually they will increase them.

IV. DIMETHYL ETHER AND DIMETHYL SULFIDE

A calculation was also made of the barriers hindering the internal rotation of the methyl groups in dimethyl ether and dimethyl sulfide. The results are also compared with the most recent experimental values in Table I. The agreement is not as satisfactory as desired. Examination of the electron diffraction data for dimethyl ether[15] reveals that the assigned C−O−C angle 111° has an uncertainty of ±4°. The calculation was therefore repeated taking the C−O−C angle as 107°. With this smaller valence angle a barrier of 2370 calories was calculated. While these calculations can hardly be taken as a basis for suggesting that the valence angle in methyl ether is near the lower limit of the electron diffraction results, i.e., 107°, in view of the sensitivity of the calculated barrier to the valence angle and the presence of electrons not shared in single bond, it is believed that the agreement between the experimental and calculated values is satisfactory.

Of course, adoption of a smaller valence angle for the molecules would reduce the product of the principal moments and thus necessitate a lower barrier for each methyl group to obtain agreement with the experimental data. Thus, reduction of the valence angle tends to improve the agreement by moving both the value calculated by this method and that calculated from the third law, spectroscopic and molecular data towards an intermediate value.

A similar situation arises in the case of dimethyl sulfide. The electron diffraction measurements of Brockway and Jenkins[16] indicate that "the sulfur bond angle in this compound is very probably between 100° and 110°." The angle used in our calculations was 102°, the same as that used by Osborne, Doescher, and Yost[12] in their calculations of the experimental barrier. Here again the discrepancy may perhaps be overcome by assuming a smaller valence angle. We have, however, not attempted a calculation on the basis of a smaller angle.

V. PROPYLENE

Propylene is the only olefin for which a calculation has been performed by this method. Whereas the experimental barrier is 2120,[17] the calculated value is 930 calories. Here again the extra pair of electrons may have an effect.

VI. METHYL AMINE, METHYL ALCOHOL, METHYL MERCAPTAN, AND ACETONE

The last four rows of Table I compare experimental barriers for methyl amine, methyl alcohol, methyl mercaptan, and acetone with those calculated by the empirical method.

The first experimental estimate of the methyl amine barrier[18] was made using spectroscopic data which were incomplete and have since been superseded by the complete assignment of Owens and Barker based on their infra-red data.[19] A recalculation of the free rotational plus the

[15] See reference j, Table I.

[16] See reference h, Table I.
[17] See reference n, Table I.
[18] See reference o, Table I.
[19] R. G. Owens and E. F. Barker, J. Chem. Phys. **8**, 229 (1940).

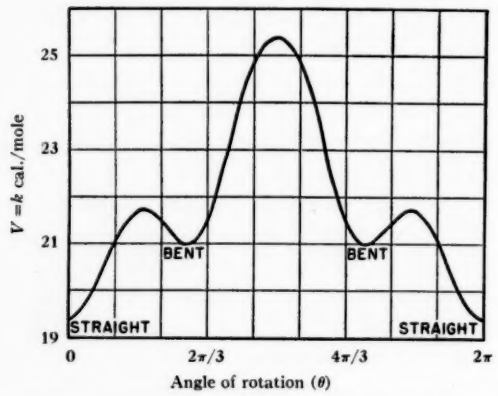

FIG. 1. The potential energy of the hydroxyl group in ethyl alcohol.

vibrational entropy using this assignment yields a value for the ideal gas at the normal boiling point 266.84°K and 1 atmos. 57.73 e.u. compared to the experimental value of 56.42 e.u. Using Pitzer's method[20] a difference of 1.31 e.u. corresponds to a hindering potential of 3000 cal. taking the reduced moment of the internal rotation as 1.92×10^{-40} g cm^2. This is the first value given in Table I. The second value of 1520 cal. is calculated from a band at 270 cm^{-1} in the infra-red spectrum which was only provisionally assigned to the mode of vibration. The empirical calculation of 2925 cal. confirms the calorimetric value and is evidence against the assignment of 270 cm^{-1} to the torsion. If the interaction with non-bonded pairs is a reason for the higher experimental value for dimethyl ether, dimethyl sulfide, and propylene then one would expect a higher experimental value for methyl amine than 2925 cal. However, for methyl amine the H−N−H and H−N−C angles were taken equal to H−N−H in ammonia, namely, as 108°6′. If the actual angles are bigger the empirically calculated value would be lower and a contribution assignable to non-bonded electrons might be necessary.

In the case of methyl alcohol the discrepancy may be reduced when the experimental barrier becomes better established,[21] but the non-bonded electrons may be partly responsible as was suggested in the case of dimethyl ether and sulfide. For methyl mercaptan an analogous discrepancy is found. The discrepancy in the case of acetone is not serious in view of the uncertainty in the experimental barrier and also in the C−C−C angle which was taken as tetrahedral in the absence of other information.

VII. ETHYL AND ISOPROPYL ALCOHOLS

The method applied thus far to methyl groups may be extended to other internally rotating groups. The application of this method to the hydroxyl group in ethyl alcohol has been given in a preliminary communication.[22] Figure 1 is a graph of the potential energy of the hydroxyl group in ethyl alcohol as a function of the angular displacement calculated by the above method. This graph has three minima and three maxima. The middle maximum ($\theta=\pi$) is higher than the other two equal maxima, and the two equal minima, $\theta=104°$, 256° adjacent to this highest maximum, are higher than the third minimum at $\theta=0$.

To obtain an approximate partition function corresponding to Fig. 1, the molecule is treated as three forms corresponding to the three minima, one straight (the lowest, $\theta=0$ in Fig. 1) and two bent ($\theta=104°$, 256°), which are optical isomers of each other. The difference in $E_0°$ (heat of formation at the absolute zero) is calculated to be $\Delta E_0°=1560$ cal./mole, by subtracting the potential energy of the lower minima (bent forms), from that of the higher minima (straight form). The "composition" has to be estimated

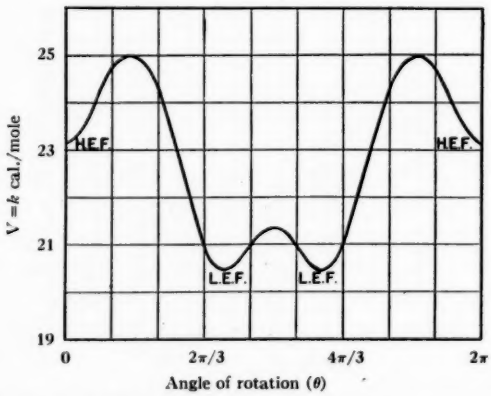

FIG. 2. The potential energy of the hydroxyl group in isopropyl alcohol.

[20] K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. **10**, 428 (1942).
[21] See reference q, Table I.
[22] J. G. Aston, G. J. Szasz, and S. Isserow, J. Chem. Phys. **11**, 532 (1943).

at each temperature from

$$\Delta F^\circ = \Delta E_0^\circ + \Delta(F^\circ - E_0^\circ), \qquad (6)$$

where the value of $F^\circ - E_0^\circ$ for each form is calculated as usual. The rest of the calculation is then like that used by Pitzer[7] for *n*-butane, which includes the entropy of mixing of the forms. It should be noted Pitzer originally took ΔE_0° as zero which is not the case here. The data used were essentially those employed in the earlier calculations on ethyl alcohol.[23] The same "average" moment was used for both forms together with the previous vibrational assignment; the only change made in the frequency assignment was the use of 985 cm^{-1} [24] for the average of the six δ frequencies, instead of 905 cm^{-1}.

The following values have been used in the calculations for restricted rotation:

	V_{CH_3}	V_{OH}
"Straight" form	1800 cal.	2375 cal.
"Bent" form	3000 cal.	4410 cal.

$$I_{CH_3} = 4.83 \times 10^{-40} \text{ g cm}^2,$$
$$I_{OH} = 1.40 \times 10^{-40} \text{ g cm}^2.$$

The barriers for the hydroxyl group were estimated from Fig. 1. The difference between the potential energy of a minimum and an adjacent maximum is the barrier hindering the rotation of the hydroxyl group past the angular position corresponding to the maximum. The barriers for the methyl groups were thus calculated by the method given in Section II to be 1070 cal. for the straight and 2500 cal. for the bent form. These values were arbitrarily enlarged by the average difference between the calculated and experimental values for other oxygen containing compounds. The calculation and comparison of the entropies are summarized in Table III.

The equilibrium in the reaction

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$$

has been discussed previously.[25]

The new value used for ΔE_0° of formation of ethyl alcohol from its elements is $-52{,}060$ cal./mole. The free energy changes recalculated at several temperatures, using this value in conjunction with the data for ethylene and water, are summarized in Table IV. The agreement between the experimental and calculated values is excellent. Although the previous agreement confirmed the presence of hindering potentials, the curves for experimental and calculated log K crossed. The new values show no such trend.

TABLE III. The entropy of ethyl alcohol from molecular data.

	351.5°K		403.2°K	
	Straight	Bent	Straight	Bent
S_{T+R}	61.03	62.41*	62.20	63.58*
S_{vib}	2.77		3.85	
$S_{f(CH_3)}$	3.67		3.80	
$S_{f(OH)}$	2.44		2.58	
$(S-S_f)_{CH_3}$	−0.58	−1.15	−0.48	−0.96
$(S-S_f)_{OH}$**	−0.71	−1.37	−0.59	−1.24
S	68.62	68.77	71.36	71.61
% present	88	12	84	16
Mixing	0.73		0.87	
S_T°	69.4		72.3	
3rd law entropy†	69.8		72.1	

* S_{T+R} includes the entropy of mixing for the optical isomers, but does not include the rotational entropy of the methyl and hydroxyl groups.
** $S_f = R(-0.775 + \frac{1}{2} \ln T + \frac{1}{2} \ln I_{red} \times 10^{40} - \ln n)$. Placing $n = 3$ limits the rotation to one-third of a revolution.
† See reference 23 of text.

TABLE IV. The free energy change and the equilibrium constant in the reaction

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g).$$

	Experimental		Calc. (previous)*		Calc. (this research)	
$T°K$	$\Delta F°$	$\log_{10} K$	$\Delta F°$	$\log_{10} K$	$\Delta F°$	$\log_{10} K$
298.2	−1200	+0.88	−1630	+1.20	−1705	+1.25
351	+315	−0.20	−350	+0.22	−362	+0.22
403	+1800	−0.98	+1570	−0.85	+1457	−0.79
600	+7480	−2.72	+7700	−2.80	+7460	−2.72

* See reference 25 of text.

It is probably significant that the removal of the necessity for ridiculously high barriers for the hydroxyl group has resulted in a better agreement with experiment. Obviously every case with an unsymmetrical barrier should at least be treated in this approximate fashion, e.g., acetic acid,[26] compounds with one unsymmetrical rotating group substituted in ethane, etc.

A compound of this type is isopropyl alcohol. Treatment of the rotation of the hydroxyl group in isopropyl alcohol according to the approximate method yields potential energies during rotation as shown in Fig. 2. To obtain a partition function three forms are taken to correspond to the three

[23] S. C. Schumann and J. G. Aston, J. Chem. Phys. **6**, 480 (1938).
[24] B. P. Dailey and W. A. Felsing, J. Am. Chem. Soc. **65**, 44 (1943).
[25] J. G. Aston, Ind. Eng. Chem. **34**, 514 (1942).
[26] J. O. Halford, J. Chem. Phys. **10**, 582 (1942).

potential energy minima; a high energy form (H.E.F. $\theta=0$) and two low energy forms (L.E.F. $\theta=140°, 220°$). The latter two are optical isomers. The difference in $E_0°$ between the high and low energy forms is estimated to be 2700 calories per mole. The "composition" has to be calculated at each temperature from (6). The rest of the calculation follows that used for ethyl alcohol. The same "average" moment was used for both forms as in the earlier treatment of Schumann and Aston.[27] The only change made in the earlier frequency assignment was the use of 1100 cm^{-1} for the average of the seven δ frequencies.[24] The following values of the potentials and reduced moments have been used in the calculation of terms due to restricted rotation:

	V_{CH_3}	V_{OH}
High energy form	3500 cal.	1850 cal.
Low energy form	3500 cal.	900 cal.

$$I_{CH_3}=5.07\times10^{-40}\text{ g cm}^2,$$
$$I_{OH}=1.40\times10^{-40}\text{ g cm}^2.$$

The barriers for the methyl group were taken as 3500 calories by analogy with isobutane. The barrier for the hydroxyl group was taken from the curve in Fig. 2 using the same procedure as for ethyl alcohol. The calculation of the entropy and the comparison of it with the experimental value are given in Table V.

TABLE V. The entropy of isopropyl alcohol from spectroscopic and molecular data at 355.5°K.

S_{T+R}*	65.48
S_{vib}	5.42
$S_{f\,CH_3}$	7.66
$S_{f\,OH}$	2.45
$(S-S_f)_{CH_3}$	−2.66
$(S-S_f)_{OH}$**	−0.17
S_{mixing}	+0.10
$S°_{calc}$	78.29 e.u.
$S°_{calorimetric}$†	78.28 e.u.

Composition: L.E.F. =99.1%, H.E.F. =0.9%.
Assumed no H.E.F. in calculation.
* S_{T+R} includes the entropy of mixing of the optical isomers.
** $S_f=R(-0.775+\frac{1}{2}\ln T+\frac{1}{2}\ln I_{red}\times10^{40}-\ln n)$. Placing $n=3$ limits the rotation to one third of a revolution.
† See reference s, Table I.

TABLE VI. The heat capacity of isopropyl alcohol vapor.

T°K	Cp exp.*	Cp calc.
427.9	28.4	29.35
457.7	30.5	30.80
480.3	32.4	31.86

* See reference 28 of text.

[27] See reference s, Table I.

TABLE VII. The free energy change and the equilibrium constant in the reaction
$(CH_3)_2CO(g)+H_2(g)\rightleftharpoons(CH_3)_2CHOH(g)$.

	Calculated composition of isopropyl alcohol		Experimental*		Calculated	
T°K	H.E.F.	L.E.F.	$\Delta F°$	$\log_{10}K$	$\Delta F°$	$\log_{10}K$
355.5	0.9%	99.1%	—	—	−3391	+2.09
450	2.0%	98.0%	−1145	+0.56	−779	+0.38
500	2.8%	97.2%	+411	−0.18	+630	−0.28

* See reference 29 of text.

The heat capacity of isopropyl alcohol vapor has been measured by Parks and Shomate.[28] Their experimental values and the values calculated from the molecular data given above are compared in Table VI. As can be seen, the agreement is not as satisfactory as desired. The fact that the experimental curve has a different slope in this region indicates that the experimental data may be in error.

The equilibrium in the reaction

$$(CH_3)_2CO(g)+H_2(g)\rightleftharpoons(CH_3)_2CHOH(g)$$

has been discussed previously.[29] The heat of this reaction, namely, −13,426 cal./mole at 355°K, has been accurately determined by Dolliver, Gresham, Kistiakowsky, Smith, and Vaughan.[30] From these data and the relation

$$\frac{\Delta E_0°}{T}=\frac{\Delta H°}{T}-\frac{\Delta(H°-E_0°)}{T}$$

$\Delta E_0°$ has been found to be −11,586 calories per mole. The free energy changes calculated at several temperatures from this value in conjunction with the data for acetone and hydrogen[31] are summarized and compared with those of Parks and Kelley in Table VII. The agreement between the experimental and calculated values is satisfactory.

[28] G. S. Parks and C. H. Shomate, J. Chem. Phys. **8**, 429 (1940).
[29] G. S. Parks and K. K. Kelley, J. Phys. Chem. **32**, 734 (1928). See also reference s, Table I.
[30] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith, and W. E. Vaughan, J. Am. Chem. Soc. **60**, 440 (1938).
[31] See reference s, Table I.

VIII. NORMAL PARAFFINS

An obvious extension of these calculations leads to the calculation of the change in potential energy as one ethyl group rotates with respect to the other in *n*-butane assuming no other interaction than that of hydrogen atoms. Figure 3 is a graph of the potential energy plotted against the angle of rotation taking the reference point ($\theta=0$) as the so-called "straight" modification. This curve leads to the conclusion that most of the hydrocarbon would be in the straight form. Whitcomb, Nielsen, and Thomas[32] have calculated the active normal modes of gaseous *n*-undecane assuming only the straight form and obtained excellent agreement with the spectrum. Cleveland and Murray[33] have measured the Raman spectrum of liquid 1-bromododecane and have concluded that the number of lines indicates the presence of only one form, thus confirming the results obtained by Whitcomb, Nielsen, and Thomas. Moreover, Kohlrausch and Köppl[34] have pointed out that the infra-red spectrum of gaseous *n*-butane has much fewer lines than would be expected if forms of symmetry lower than C_{2h} were present in appreciable quantities. On the other hand, Kohlrausch and Köppl have used the Raman spectrum of the liquid to show that the straight and bent forms are present. Mizushima, Morino, and Nakamura[35] have confirmed these conclusions by showing that certain lines disappear altogether in the spectrum of the solid while others remain, indicating that the bent form passes over into the straight form in the solid. It may well be that the forces in the liquid allow a stability of the bent form due to molecular interaction. The situation, however, is not clear.

By fitting a curve of the type

$$V=\tfrac{1}{2}V_0(1-\cos 3\theta)$$

to the calculated potential curve near the position of minimum energy, the barrier associated with the lower energy levels of the oscillation in the straight form of *n*-butane would be about 3000 calories.

Pitzer[36] has obtained excellent agreement with experiment using a very logical but semi-empirical treatment for long chain hydrocarbons. This treatment assumes very much less preference for the straight form of the hydrocarbon than indicated by Fig. 3, an assumption justified by the spectrum of the liquid. It is therefore of interest to see if the thermodynamic data can be fitted by the assumption of the straight form alone. To do this the average value of the carbon-carbon bending frequencies must be adjusted to give the correct value of the entropy at one temperature and the rocking frequencies of the methyl groups must be chosen to fit the heat capacity curves in the gas. The barrier hindering internal rotation of the end methyl groups was taken as 3000 calories in keeping with the previous calculations while that of the mutual oscillation of higher alkyl groups was taken as 3000 calories for the reason given above in the case of the ethyl groups in *n*-butane.

Only in the case of *n*-butane were detailed spectroscopic data available.[34,37–41] These data were assigned as follows to get the best fit with experiment:

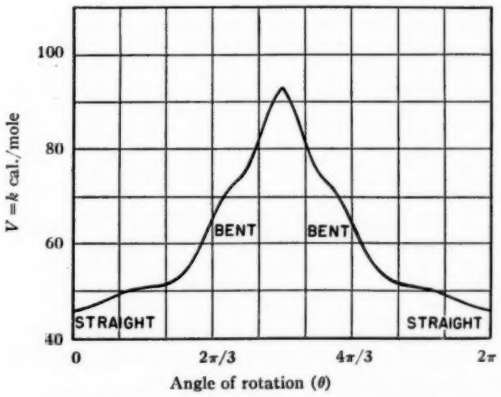

FIG. 3. The potential energy of the ethyl groups in *n*-butane.

[32] S. E. Whitcomb, H. H. Nielsen, and L. H. Thomas, J. Chem. Phys. **8**, 143 (1940).
[33] F. F. Cleveland and M. J. Murray, J. Chem. Phys. **8**, 867 (1940).
[34] K. W. F. Kohlrausch and F. Köppl, Zeits. f. physik. Chemie **B26**, 209 (1934).
[35] S. Mizushima, Y. Morino, and S. Nakamura, Tokyo Inst. Phys. Chem. Res. **37**, 208 (1940).
[36] K. S. Pitzer, J. Chem. Phys. **8**, 711 (1940).
[37] Ananthakrishnan, Proc. Ind. Acad. **A5**, 285 (1937).
[38] S. Bhagavantam, Ind. J. Phys. **6**, 595 (1932).
[39] W. W. Coblentz, Investigations of Infra-Red Spectra, Carnegie Inst. Pub. **35**, 142 (1905).
[40] P. Lambert and J. Lecomte, Ann. de physique **10**, 566 (1938).
[41] J. W. Murray and D. H. Andrews, J. Chem. Phys. **1**, 406 (1933).

TABLE VIII. Comparison of experimental and calculated entropies for gaseous normal paraffins.

T°K	$S_{(exp)}$	$S_{(calc)}$
n-butane		
210.00	67.05[a]	66.88
230.00	68.60	68.62
272.66	72.05	72.16
n-pentane		
298.16	83.13[b]	83.24
n-heptane		
298.16	101.54[c]	102.00
371.5	111.78[d]	111.59

[a] J. G. Aston and G. H. Messerly, J. Am. Chem. Soc. **62**, 1917 (1940). The entropy values at 210.00 and 230.00°K were calculated in the usual manner from the data given in this paper.
[b] See reference 42 of text.
[c] See reference 36 of text.
[d] K. S. Pitzer, J. Am. Chem. Soc. **62**, 1224 (1940).

Carbon chain bending: 240 (2).
Carbon chain stretching: 837, 893, 1059.
Hydrogen rocking: 954, 980, 1003, 1041, 1050, 1123 (3), 1146 (2).
Hydrogen bending and stretching: 1282, 1300, 1450 (6), 2861, 2939 (4), 2965, 2978 (2), 3000 (2).

For *n*-pentane the frequency assignment was that of Messerly and Kennedy[42] except that the bending frequencies at 250 (1) and 326 (2) cm^{-1} were replaced by three at 192 cm^{-1} and the thirteen hydrogen rocking frequencies at 950 cm^{-1} were changed to thirteen at 1070 cm^{-1}. For *n*-heptane the frequency assignment was the following schematic one:

Carbon chain bending: 165 (5).
Carbon chain stretching: 1000 (6).
Hydrogen rocking, bending and stretching: 1070 (19), 1400 (11), 3000 (16).

The assignments chosen are self-consistent except for the carbon-carbon bending frequencies chosen to fit the thermodynamic data. The calculated values of the entropy are compared with experiment in Table VIII while the heat capacity values are compared in Table IX.

The significant fact about the average carbon-carbon bending frequencies is their decrease with the increase in the length of the chain. This decrease is roughly according to the square root of the mass. The values are: *n*-butane, 240 (214); *n*-pentane 192; *n*-heptane 165 (163). The values given in parentheses are calculated from the *n*-pentane value assuming inverse proportionality to the square root of the mass. Kassel[43] finds bending frequencies whose algebraic average values are: *n*-butane 323 (338); *n*-pentane 302; *n*-heptane 285 (256). The values in parentheses have the same relative significance as above.

[42] G. H. Messerly and R. M. Kennedy, J. Am. Chem. Soc. **62**, 2988 (1940).

TABLE IX. Comparison of experimental and calculated heat capacities for gaseous normal paraffins.

T°K	$C_{p(exp)}$	$C_{p(calc)}$
n-butane		
400	29.94[a]	29.95
500	35.67	35.80
600	40.68	40.65
700	44.73	44.87
n-pentane		
331	31.26[b]	31.58
371	34.4	34.90
427	38.0	38.71
n-heptane		
423	53.9[c]	53.14
450	57.5[d]	56.57

[a] See reference 24 of text.
[b] K. S. Pitzer, J. Am. Chem. Soc. **63**, 2413 (1941).
[c] See reference d, Table VIII.
[d] A. Eucken and B. Sarstedt, Zeits. f. physik. Chemie **B50**, 143 (1941). Chem. Abs. **37**, 2648 (1943).

IX. EFFECT OF OTHER ATOMS BESIDES HYDROGEN

It has been found[44,45] that 1,1,1-trifluoroethane and 1,1,1-trichloroethane have barriers of 3450 and 2700 cal., respectively, hindering the internal rotation of methyl groups. These barriers must be due to interaction of hydrogen with the fluorine and chlorine atoms, respectively, or with the electrons in the bonds joining these atoms to carbon. There is no *a priori* reason to assume that the interaction is one of repulsion but this can be ascertained experimentally by studies of the mono and 1,1-dihalogen derivatives which will have barriers of about 3000 cal. if the interaction due to the halogen atoms corresponds to repulsion but only of about 1000 cal. if this interaction be one of attraction. Experiments on ethyl chloride and ethylidene dichloride will be carried out in this laboratory as soon as the opportunity arises.

[43] L. S. Kassel, J. Chem. Phys. **3**, 326 (1935).
[44] H. Russell, Jr., D. R. V. Golding, and D. M. Yost, J. Am. Chem. Soc. **66**, 16 (1944).
[45] T. R. Rubin, B. H. Levedahl, and D. M. Yost, J. Am. Chem. Soc. **66**, 279 (1944).

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Magnetic Studies of Chromium Oxide Catalysts

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The magnetic susceptibility of active chromium oxide gel and "glowed" inactive chromium oxide was measured from liquid air temperature to 444°C and no difference in magnetic behavior was noted. Activated adsorption of hydrogen does not markedly affect the magnetic susceptibility of the active gel catalyst. The interaction of chromic nitrate with ammonia, filtration, and drying results in a chromium oxide intermediate in oxygen content to Cr_2O_3 and CrO_3. Revivification of the catalyst by oxygen treatment results in a similar chromium oxide. Mechanism for the preparation of an active chromium oxide catalyst and a structure for such an oxide have been proposed.

CHROMIUM oxide gel obtained by slow interaction in dilute solution of chromic nitrate and ammonia has been found to be an efficient catalyst in various hydrogenation-dehydrogenation reactions of hydrocarbons. This gel catalyst is unstable with respect to crystalline chromic oxide and reverts to the latter undergoing "the glow phenomenon." The crystalline chromic oxide so obtained is inactive for reactions for which the gel form is active.[1] Differentiation between the two forms by chemical analysis is complicated by the fact that it is difficult to distinguish between the oxygen held in the water of hydration and the oxygen associated directly with the chromium atom due to a valence of chromium greater than three. It was therefore thought of interest to see whether the differences in catalytic properties between the gel and the crystalline form reflected itself in differences in magnetic characteristics. A magnetic study was also made of substances obtained at various stages of the preparation of standard chromium oxide gel catalyst.

MATERIALS

Sample A1

Standard chromium oxide gel was prepared by slow precipitation of chromic nitrate with dilute ammonium hydroxide solution. The product was washed free of ammonium and nitrate ions, filtered, and dried overnight at 110° C.[2]

Sample A2

The product A1 was reduced by purified hydrogen at 475°C until no more water was formed. The sample was then pumped off by a mercury diffusion pump at 475°C for three days to remove the adsorbed hydrogen. It was then cooled to room temperature and purified nitrogen was introduced.

Sample A3

The product A1 was reduced by a stream of hydrogen at 475°C until no more water was formed and, to insure chemisorption of hydrogen, cooled to room temperature in the course of twenty-four hours in hydrogen.

Sample A4

The product A1 was reduced *in situ* in a catalytic reaction vessel and used for the dehydrogenation of *n*-heptane to toluene until the catalyst was thoroughly poisoned. The catalyst was then treated for twelve hours with nitrogen containing about 2 percent oxygen to burn off the carbon deposited on the surface. The catalyst was cooled in nitrogen.

Sample B1

This sample was chromium oxide prepared by the interaction of one molar solution of ammonium hydroxide and chromic nitrate at 100°C, repeated washings, filtration, drying, and reduction with hydrogen slowly raising the temperature to 450°C. It should be noted that during the careful reduction with hydrogen, the oxide

[1] Turkevich, Fehrer, and Taylor, J. Am. Chem. Soc. **63**, 1129 (1941).
[2] V. Kohlschutter, Zeits. f. anorg. u. allgem. Chemie **220**, 370 (1934).

underwent a glow phenomenon at about 150°C and that the resultant product was an inactive "crystalline" form of chromium oxide.

PROCEDURE

The magnetic susceptibilities were determined by the Gouy method using the apparatus described by Turkevich and Selwood.[3] Temperatures above room temperature were obtained by appropriate vapor baths.

EXPERIMENTAL RESULTS AND DISCUSSION

The results of the magnetic measurements are given in Table I. None of the samples studied was ferromagnetic in the temperature range studied.

Comparison of the results obtained on active sample A3 and inactive sample B1 shows that within the error of the magnetic measurement, there is no difference in the magnetic susceptibility between the active and inactive forms. These two forms show, however, marked differences in catalytic activity[1] and in hydrogen adsorption characteristics.[4]

Comparison of measurements obtained with samples A2 and A3 shows that activated adsorption has little effect on the susceptibility of chromium oxide in the temperature range studied.

The values obtained on samples A2, A3, and B1 agree well both in absolute value and temperature dependence with the results reported in the literature for Cr_2O_3.[5]

Measurements on samples A1 and A4, samples obtained before hydrogen reduction and after treatment with oxygen, respectively, reveal a marked difference in magnetic characteristics from the samples previously examined. The values of the magnetic susceptibility are higher and markedly temperature dependent, suggesting the identification of these samples with oxides intermediate in oxygen content to Cr_2O_3 and CrO_3. There has been considerable confusion concerning such oxides, but recent investigation of Bhatnagar, Cameron *et al.*[5] reports the existence of a dioxide and two non-stoichiometric oxide ranges $CrO_{2.6-2.2}$ and $CrO_{1.9-1.7}$, the values of magnetic susceptibility for the different samples lying between 42.2 and 26.9×10^{-6}. Their magnetic measurements on the effect of oxygen and hydrogen were less conclusive than those obtained in this investigation because they measured this effect at one temperature and also because the chromium oxide they used was of inferior catalytic activity than the gel standard form.

On the basis of the results of this investigation the following mechanism for the formation of the active chromium oxide catalyst is suggested: The precipitation, washing, filtration, and drying at 110°C of the product of interaction of chromic nitrate and ammonia result not in the formation of a hydrate of chromium sesquioxide but of a hydrate of an oxide higher in oxygen content than that demanded by the formula Cr_2O_3. This oxygen is removed from the solid by hydrogen reduction. The process of catalyst revivification[6] results not only in the removal of carbon from the surface but also in a reoxidation of the catalyst to this higher oxide. Since it has been established that the catalytic activity is not impaired by the revivification process, the active catalyst must have sufficient open structure to accommodate this oxygen. This view has been substantiated by the preparation of a very active catalyst by the reduction of chromic acid to an "intermediate" oxide by alcohol, drying, and final reduction with hydrogen.[1]

TABLE I. Specific susceptibilities $\times 10^6$ of chromium oxides.

	90	184	273	373	457	575	707°K
A1	—	54	41	37	—	—	—
A2	21	19	21	—	—	—	—
A3	20	19	21	22	21	19	18
A4	—	40	35	—	—	—	—
B1	21	20	21	22	21	19	18

[3] J. Turkevich and P. C. Selwood, J. Am. Chem. Soc. **63**, 1077 (1941).

[4] R. L. Burwell and H. S. Taylor, J. Am. Chem. Soc. **58**, 1753 (1936).

[5] S. S. Bhatnagar, A. Cameron, E. H. Harbard, P. L. Kapur, A. King, and B. Prakash, J. Chem. Soc., p. 1437 (1939).

[6] D. J. Salley, H. Fehrer, and H. S. Taylor, J. Am. Chem. Soc. **63**, 1131 (1941).

Energies of Solution of Silica in Water and HCl

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THE solubilities of silica in water and acid at various temperatures evidently depend upon the energies of association and dissociation of the various ions present, energies which are derivable from the solubilities by thermodynamic analysis. Recent determinations by Harned[1] of the dissociation constant of water at various temperatures, by Hitchen[2] of the solubility of silica through a range of elevated temperatures, and by Lenher and Merrill[3] on its solubility in solutions of hydrochloric acid of 0 to 20 percent concentration appear to be of sufficient precision to warrant such reductions but none such seems to have been made. The work was done for its bearing on problems concerned with the solubilities of silicates in general and is here summarized to save needless repetition. Many of the associations involved, such as that of water molecules for its ions and of silica molecules for each other (polymerization), represent energies negligible in comparison with those considered.

With the ionization constant K_w of water known for a range of temperatures, the energy necessary to separate H and OH ions in water may be readily calculated in calories per mole. Hitchen's data on solubility in water likewise give the heat of solution of silica in water. From the depression of solubility by acid the work done by the acid may be calculated. A comparison of these three energies is of interest.

Harned's observed values of K_w are given in Table I with values for 70 and 90°C added, calculated from

$$\log_e K_w = -11038.1/T - 7.13954 \log_e T - 0.023892T + 84.8291 \quad (1)$$

which, with the relation $E = -Rd \log K/d(1/T)$ and $R = 1.9864$, gives

$$E_k = -21926 + 14.182T + 0.047460T^2, \quad (2)$$

values of which are also given in Table I.

Hitchen's data on silica solubility S in grams per liter and heat of solution E_s in calories per mole are also given in Table I.

$$\log S = -8168.78/T - 35.7430 \log T + 0.045306T + 215.8447, \quad (3)$$

$$E_s = -16226.47 + 71.0000T - 0.090000T^2. \quad (4)$$

It is to be noted that $E_w - E_s$ is sensibly constant, 6800 cal./mole. However, each molecule of SiO_2 takes on two molecules of H_2O before dispersing as a solution. Since $E_w - E_s$ is much more nearly constant than $2E_w - E_s$, it is to be inferred that most of the energy change is due to the first H_2O taken on during the hydration of the silica, the second H_2O differing little in energy from the solvent. The useful energy equation (not exact) is therefore $E_w = E_s + 6800$ cal./mole of water.

TABLE I. Dissociation constants of water and solubilities of silica in water, with energies.

T	K_w	E_k	S	E_s	E_w	$E_w - E_s$
0	0.1133	−14511	0.110	−3547	10187	6640
15	0.4503	13898	.153	3240	10013	6773
30	1.468	13265	.202	2975	9844	6869
50	5.474	12386	.270	2680	9605	6925
70	16.16	11470	.337	2456	9361	6905
90	39.31	10519	.409	2311	9107	6796

$K_w \times 10^{-14}$, dissociation constant of water (Harned).
S, solubility of silica in water in grams per liter (Hitchen).
E_k calories per mole to separate H and OH in H_2O.
E_s, net heat of solution of SiO_2 in H_2O in calories per mole.
E_w, energy of association of H_2O molecules with each other in liquid (cal./mole). Internal latent heat.

DEPRESSION OF SILICA SOLUBILITY BY ACID

The solubility of silica in hydrochloric acid of various concentrations determined by Lenher and Merrill in 1917, falls off in a smooth curve from 418 p.p.m. in pure water to 25 p.p.m. in 20 percent acid. No attempt at a thermodynamic treatment of their determinations appears ever to have been made, nor even to formulate them in a specific law. Such discussion and formulation seem well worth while in view of their fundamental bearing on the problem of the solubility of silicates in general. The data of Lenher and Merrill are given in Table II.

[1] Herbert S. Harned, J. Frank. Inst. **225**, 642 (1938).
[2] C. S. Hitchen, *The Solubility of Silica in Water*, Bulletin 364 of the British Institute of Mining and Metallurgy (January, 1935).
[3] V. Lenher and H. B. Merrill, J. Am. Chem. Soc. **39**, 2630 (1917).

TABLE II. Solubility of silica in HCl solutions.

Acid percent	Silica dissolved	S_0/S	log S_0/S	Acid percent	Silica dissolved	S_0/S	log S_0/S
	p.p.m.				p.p.m.		
0.0	418	1.000	0.0	7.6	230	1.8174	0.5974
1.2	408	1.0245	.0242	9.3	190	2.2000	0.7885
3.0	374	1.1176	.1111	10.0	182	2.2967	0.8315
3.8	354	1.1808	.1662	13.6	112	3.7321	1.3170
5.3	302	1.3841	.3251	15.8	88	4.7500	1.5581
6.3	268	1.5597	.4445	18.6	58	7.2069	1.9750

The depression in solubility (S_0-S) is related to the acid causing it but the graph of log (S_0-S) against log (acid concentration) has a definite though slight curvature. RT log (S_0/S) is the work (in cal./mole) done in depressing the silica concentration from S_0 to S. A graph shows an excellent linear relation between this energy and HCl concentration, the equation for which is

$$\log (S_0/S) = 0.1179\ \mathrm{HCl} - 0.3031$$
$$= 0.1179\ (\mathrm{HCl} - 2.57).$$

The work done by a mole of HCl is

$$RT \log (S_0/S)$$

divided by the molar concentration of acid. The graph of this work per mole plotted against acid concentrations consists of two straight lines, steep at lower, nearly flat at higher concentrations, meeting in a rounded shoulder at about 7 percent (2 molar) HCl. It does not recall any familiar properties of this acid but is clearly descriptive of the competition of HCl and $Si(OH)_4$ ions for water. The actual energies involved are small; at 9.3 percent HCl, for example, a liter of solution contains 2.55 moles of HCl, 0.0032 mole of SiO_2, and RT log (S_0/S) is 569 cal./mole of SiO_2 or 223 cal./mole HCl. Even this small amount of extra energy is sufficient to halve the solubility of the silica and indicates the delicacy of the balance between free and associated ions.

Data on the solubility of pure silica in water and HCl solutions have been formulated and reduced to energy as a step in the study of the solubility of the silicates. Two new relations developed may prove to be of general interest.

Letters to the Editor

PROMPT publication of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is the third of the month. Because of the late closing date for the section no proof can be shown to authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not in general exceed 600 words in length.

Depolarization of Raman Lines

A Further Simplification of Method

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June 9, 1944

GLOCKLER and Baker[1] have studied the use of Polaroid in the measurement of the depolarization factors of Raman lines. They used a mica plate in order to rotate one of the components following the method of Stitt and Yost.[2] Lately we have realized that the mica half-wave plate is unnecessary if the two Polaroid films are positioned in front of the spectrograph so that their line of contact is at 45° to the vertical axis of the spectrograph. Preliminary results seem to show that this method will work satisfactorily. This suggested arrangement is published now because further work will be delayed for an unknown period on account of the war.

[1] Geo. Glockler and H. T. Baker, J. Chem. Phys. **11**, 446 (1943).
[2] F. Stitt and D. M. Yost, J. Chem. Phys. **5**, 90 (1937).

Thermal Diffusion in Liquids

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A THERMAL diffusion tube similar to that described by Korsching and Wirtz[1] has been used to observe effects obtainable by varying some of the parameters involved in thermal diffusion experiments.

The tube, formed by clamping a rectangular Pliofilm gasket between two brass strips, has been previously described.[2] Since difficulty was encountered in keeping the tube liquid tight with a 100-gauge Pliofilm gasket, 450-gauge Pliofilm[3] was substituted. The diffusion column thus formed was rectangular in cross section, 1.59×0.057 cm, and 1 meter long. The average temperature difference ΔT maintained between the top and bottom sides of the tube was 49°C.

TABLE I.

Molar concentration of $ZnSO_4$	Time in hours	Tube slope in degrees	C_B/C_T
0.6	2	45	3.70
0.6	4	45	4.97
0.6	8	45	10.8
0.6	12	45	17.1
0.4	2	45	3.04
0.6	2	45	3.70
0.8	2	45	2.85
0.6	2	6	2.55
0.6	2	15	2.87
0.6	2	30	3.28
0.6	2	45	3.70
0.6	2	60	3.62
0.6	2	75	3.09
0.6	2	85	2.71

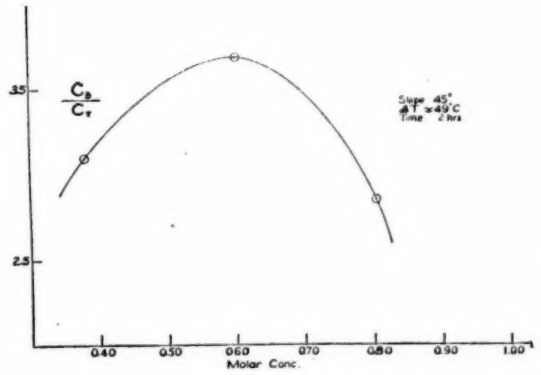

FIG. 1.

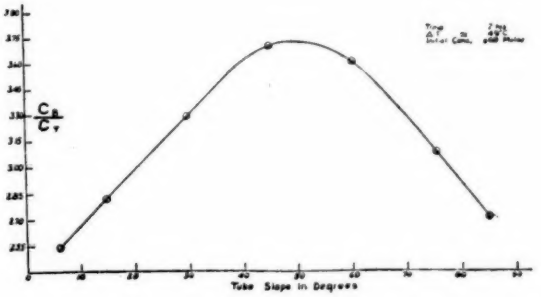

FIG. 2.

Solutions of $ZnSO_4$ were used throughout the investigation since they had been previously shown to give a large effect.[1] Analyses of concentration were made by measurement of the refractive index.

The results are given in Table I. The effected separation is expressed as the ratio of the molar concentration C_B of a sample taken from the bottom of the tube to the concentration C_T of a sample from the top.

Figures 1 and 2 are graphs of data taken from Table I. They show more clearly the maxima obtained.

[1] Korsching and Wirtz, Naturwiss. **27**, 367 (1939).
[2] H. Carr, Phys. Rev. **61**, 726A (1942).
[3] Kindly supplied by the Goodyear Rubber Company, Akron, Ohio.